

# Adsorption and Desorption Processes of Chromium Ions Using Magnetic Iron Oxide Nanoparticles and Their Relevant Mechanism

M. Jadidi, N. Etesami\*, M. Nasr Esfahany

Department of Chemical Engineering, Isfahan University of Technology, Isfahan, Iran

---

## ARTICLE INFO

### Article history:

Received: 2016-07-05

Accepted: 2016-10-26

---

### Keywords:

Heavy Metals

Adsorption

Iron Oxide Nanoparticles

Desorption

Adsorption Mechanism

---

## ABSTRACT

*In this study, adsorption of Cr(VI) from aqueous solution by Fe<sub>3</sub>O<sub>4</sub> nanoparticles was investigated. Desorption process and recovery of nanoparticles using different solutions were then carried out, and it was observed that NaOH (0.5M) can remove 90 % of adsorbed chromium ions. Following the completion of adsorption/desorption cycles, it was determined that nanoparticles have still had a high ability of chromium ions adsorption after 4 cycles. In addition, it was found that when iron oxide nanoparticles are washed with NaOH solution, the adsorption efficiency increases in the next cycle. FTIR spectra and zeta potential analyses demonstrated the increase in the positively charged surface of nanoparticles leads to increased electrostatic attraction forces between the iron oxide nanoparticles and chromium ions, which finally resulted in the adsorption increase. Therefore, in this research, pretreatment of nanoparticles with NaOH solution modifies the surface of Fe<sub>3</sub>O<sub>4</sub> nanoparticles by increasing positively-charged surface mechanism, and so the adsorption efficiency has improved in the next cycle.*

---

## 1. Introduction

Pollution of water resources with heavy metals has turned into one of the most important environment's problems due to industrial developments. Heavy metals are not biodegradable and can be accumulated in living organisms; so, a large number of heavy metal ions are known to be toxic and carcinogenic [1].

Chromium is one of the most toxic heavy metals, classified in Group A carcinogen [2]. Many different methods have been used for heavy metal removal such as chemical precipitation, membrane filtration, adsorption,

ion-exchange, electrochemical treatment technologies, etc. [1, 3, and 4].

Among these methods, the adsorption process is flexible in design and operation, and in most cases, adsorption offers high removal efficiency; Moreover, one of the main advantages of the adsorption process is its reversible nature for adsorbent regeneration and multiple use of adsorbent [4,5].

Numerous studies have been done on using nanoparticles as adsorbent to adsorb heavy metals during recent years. Among all nanoparticles, iron oxide nanoparticles are

---

\*Corresponding author: netesami@cc.iut.ac.ir

widely used adsorbent [5,6]. Ease of access to resources and nanoscale synthesis, biodegradability, large surface area, surface modifiability ability, and special magnetic properties are the main features of iron oxide nanoparticles [7, 8 and 9].

Use of iron oxide magnetic nanoparticles for adsorption of chromium has been in several studies. Hu et al. [10] synthesized and evaluated maghemite nanoparticles ( $\text{Fe}_2\text{O}_3$ ) for adsorption of Cr(IV). The maximum adsorption capacity of 19.2 mg/g occurred at pH 2.5. Regeneration studies with NaOH solution underwent six adsorption-desorption processes, and the adsorption capacity of maghemite remained almost constant for the six cycles.

Chowdhury and Yanful [11] used mixed magnetite-maghemite nanoparticles in the uptake of chromium from water samples. The results of their study show 96-99 % chromium uptake under controlled pH conditions. The maximum chromium adsorption occurred at pH 2 with values of 2.4 mg/g. Wang and Lo [12] synthesized mesoporous magnetic iron-oxide ( $\gamma\text{-Fe}_2\text{O}_3$ ) for Cr(VI) removal. The maximum adsorption (89.2 %) occurred at pH 2. They used NaOH for desorption of chromium from nanoparticles, and it was found that mesoporous  $\gamma\text{-Fe}_2\text{O}_3$  retained more than 90 % of its original Cr(VI) adsorption capacity after 5 cycles.

Pang et al. [13] used PEI-modified magnetic nanoparticles in removal of Cr(IV). The maximum adsorption efficiency of 83.33 % occurred at pH 2. Regeneration studies with NaOH solution underwent six adsorption-desorption processes, and the adsorption capacity decreased only 9 % in the sixth cycle.

As noted, there are several studies on the

adsorption of chromium by iron oxide nanoparticles. In most of these studies, nanoparticles were modified with different materials to improve adsorption efficiency, and different results have been reported. However, in all of them, maximum adsorption of chromium occurred in pH range of 2-3 [14-18].

The objective of the presented study is to investigate adsorption of Cr(IV) with iron oxide nanoparticles, desorption process, and realization of the dominant mechanism in both adsorption and desorption processes. Reusability of nanoparticles in adsorption/desorption cycles and the effect of desorption process on the modification of surface of the adsorbent and adsorption efficiency were investigated too.

## 2. Materials and method

Magnetic iron oxide nanoparticles ( $\text{Fe}_3\text{O}_4$ ) with average size less than 50 nm and polyvinylpyrrolidone coating were purchased from Sigma Aldrich (USA). Potassium dichromate ( $\text{K}_2\text{Cr}_2\text{O}_7$ ), sodium hydroxide (HCl), phosphoric acid ( $\text{H}_3\text{PO}_4$ ) and sodium hydroxide (NaOH) were the products of Merck (Germany).

The adsorption of chromium anions by magnetic nanoparticles was investigated in aqueous solutions at room temperature. In general, 0.625 g of nanoparticles were mixed with 250 ml chromium solution (7 ppm, pH 2) for 270 minutes with mechanical stirrer and ultrasonic processor (UP400S model made by Hielscher Company), alternatively. Samples were pipetted at certain intervals and the adsorbent was separated using a magnet. The concentrations of chromium ions in the remaining solutions were measured using an Atomic Absorption Spectrometer (AAS), (Buck Scientific, 210VGP). Chromium

removal efficiency was calculated by Eq. 1.

$$E(\%) = \frac{C_1 - C_2}{C_1} \times 100 \quad (1)$$

where  $C_1$  is the chromium initial concentration and  $C_2$  is chromium concentration after adsorption.

In order to investigate the desorption process, after completion of the adsorption and sampling, nanoparticles were washed with distilled water, and then were mixed with desorption solutions for 270 min with mechanical stirrer. At the end, in order to determine the amount of chromium ions separated from the nanoparticles surfaces and to calculate the desorption efficiency, chromium concentration in desorption solution was measured with AAS. Desorption efficiency was calculated by Eq. 2.

$$R(\%) = \frac{C_3}{C_1 - C_2} \times 100 \quad (2)$$

where  $C_3$  is the chromium concentration in

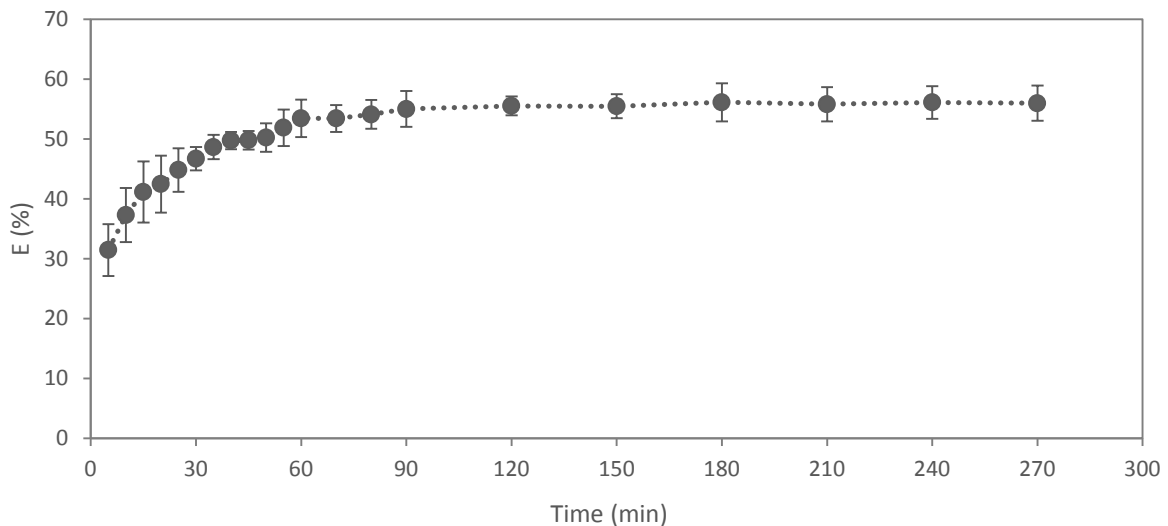
desorption solution.

Regeneration of nanoparticles as adsorbent was investigated with several desorption solutions, and the suitable solution was chosen; therefore, consecutive adsorption-desorption cycles were performed according to the process mentioned. Sampling and AAS analysis was carried out at least three times and error bars were calculated based on standard deviation, as shown in the figures.

### 3. Results and discussion

#### 3.1. Adsorption process

According to the process mentioned in section 2, adsorption tests were conducted in batch system. Samples were pipetted at certain intervals, and the amounts of the remaining chromium in solution were determined by AAS. These concentrations actually indicate the amounts of chromium that have not been adsorbed by nanoparticles. Removal efficiency of Cr(IV) during time is shown in Fig. 1.



**Figure 1.** Cr(IV) adsorption efficiency during time.

Fig.1 shows that the rate of adsorption decreases with time until it gradually approaches a plateau, because the equilibrium concentration is approached in an aqueous

solution. The high adsorption at the beginning of the process could be due to the great number of unfilled active sites on the adsorbent surface and also the high

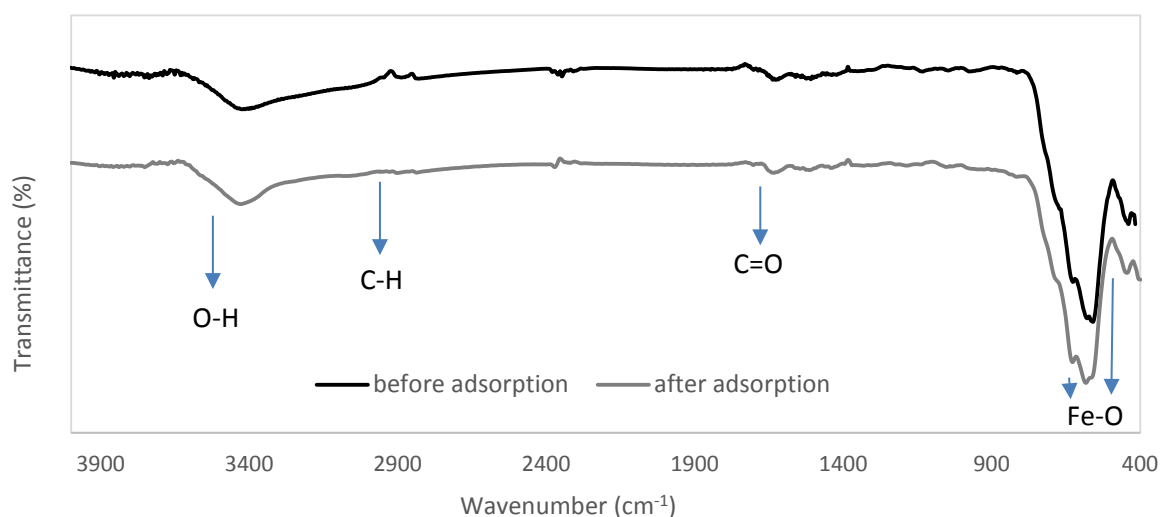
concentration of solution.

FTIR analysis of iron oxide nanoparticles before and after desorption (Fig. 2) resulted in the bonding of any chemical that has not been created between absorbent and adsorbate during adsorption process. FTIR spectra of nanoparticles before and after desorption are shown in Fig. 2. Peaks at  $439\text{ cm}^{-1}$  and  $559\text{ cm}^{-1}$  are due to metal-oxygen bonds of Fe-O stretching and bending vibration in the octahedral and tetrahedron networks. Peaks at  $1627\text{ cm}^{-1}$  represent the vibration of C=O bond of carbonyl group in the structure of PVP (nanoparticles coating).

Weak peaks at  $2852\text{ cm}^{-1}$  and  $2924\text{ cm}^{-1}$  are related to C-H group in PVP. Widescreen

band of wavelengths  $3423\text{ cm}^{-1}$  is due to the vibrations of hydroxyl O-H attached to the metal; there may also be some moisture and water molecules [19-21].

According to Fig. 2, no additional peaks in the FTIR spectrum of nanoparticles after adsorption have been generated. In fact, any chemical bond between chromium anions and nanoparticles has not been formed during the adsorption process. Thus, the adsorption mechanism of Cr(VI) onto  $\text{Fe}_3\text{O}_4$  nanoparticles is suggested to be electrostatic attraction. So, the desorption process of nanoparticles may be useful for reusing of adsorbent.



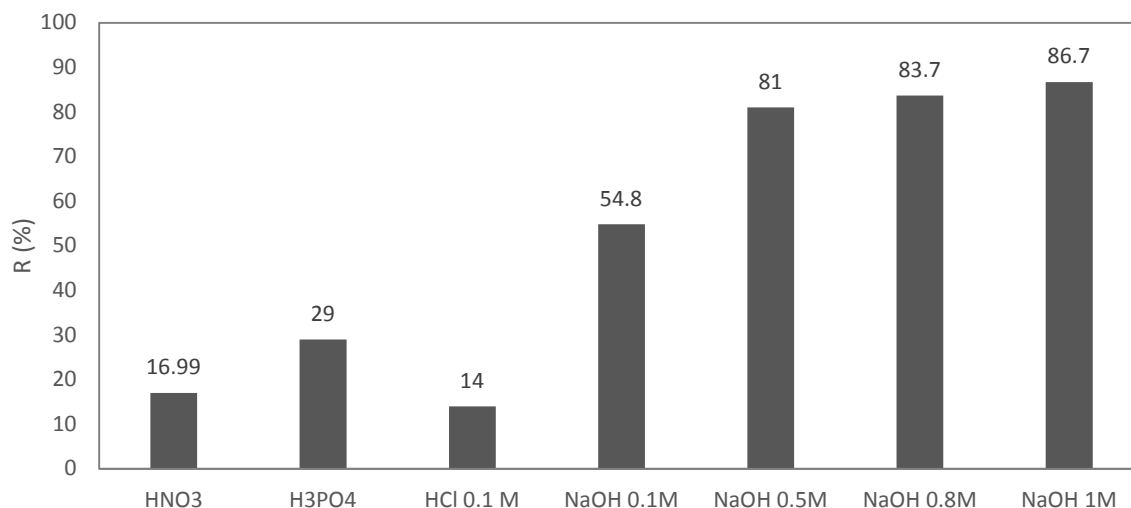
**Figure 2.** FTIR spectra of  $\text{Fe}_3\text{O}_4$  nanoparticles before and after the adsorption.

### 3.2. Desorption process

Desorption processes in accordance with the section 2 were carried out by various regenerative solutions whose results can be seen in Fig. 3.

Fig. 3 shows that HCl (0.1M),  $\text{HNO}_3$  (0.5 M), and  $\text{H}_3\text{PO}_4$  (0.5M) do not have any ability for the desorption of chromium anions from nanoparticles, while NaOH solution in all concentrations shows high ability for the desorption of chromium anions from nanoparticles. The surfaces of iron oxide

nanoparticles are covered with Fe-OH hydroxyl groups that vary in forms at different pHs. The surface charge is neutral at pH-Zero Point of Charge (pHzpc). Below the pHzpc, protonation of the nanoparticle surface leads to the formation of  $\text{Fe}-\text{OH}_2^+$ , and the adsorbent surface is positively charged, and so anion adsorption occurs. Above the pHzpc, deprotonation of the nanoparticle surface leads to the formation of  $\text{Fe}-\text{O}^-$ , and the adsorbent surface is negatively charged [9, 10].



**Figure 3.** Desorption efficiency of nanoparticles using different regenerative solutions.

Below the  $pH_{zpc}$ , anion adsorption occurs and with further decreasing of pH, adsorption increases, but if heavy metals ions are cation, adsorption increases while pH increasing. Heavy metals in aqueous solutions appear mostly in the form of cations. For this reason, the adsorption of Lead, Nickel, Copper, Cadmium, and Zinc cations occurs at pH higher than  $pH_{zpc}$ . However, chromium metal ions in aqueous solutions appear in negatively charged compounds such as  $HCrO_4^-$ ,  $Cr_2O_7^{2-}$ , and  $CrO_4^{2-}$ . Thus, the adsorption of this metal will have the maximum value in pH below the  $pH_{zpc}$  [13, 22].

As noted, the nanoparticle surface is positively charged in basic ambience, and this causes electrostatical repulsion between iron oxide nanoparticles and chromium anions, and it will also result in the release of adsorbed chromium anions.

Since the percentage of desorption at three concentrations of 5.0, 8.0, and 1M NaOH had no changes considerably, NaOH solution of 0.5M was used as a regeneration solution to save laboratory materials.

### 3.3. Adsorption/desorption cycles

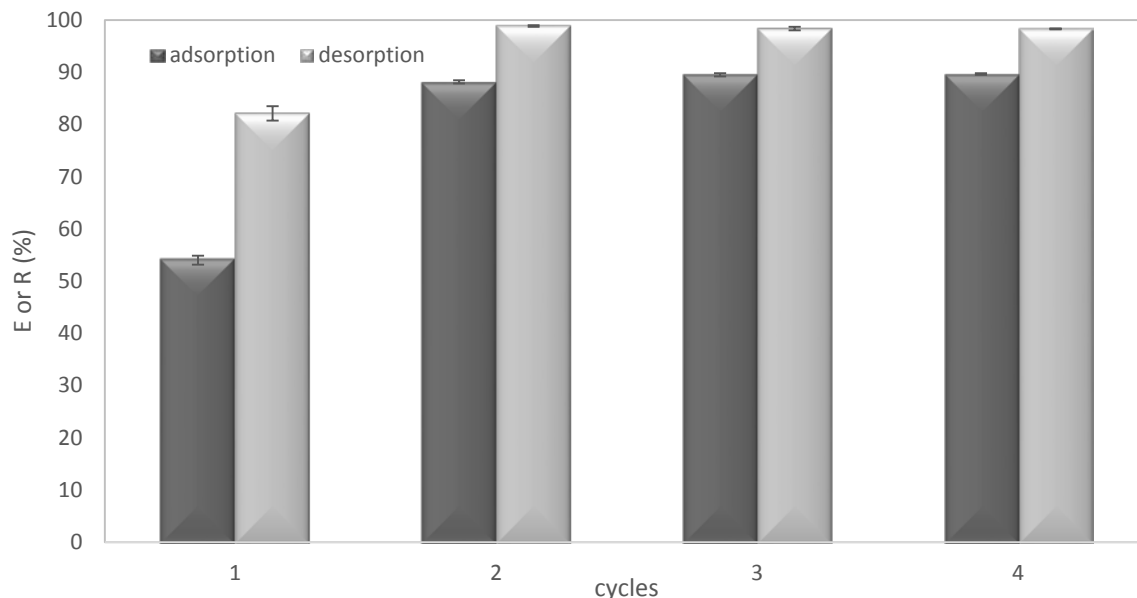
In order to investigate the ability of

regenerated nanoparticles to adsorption of chromium, adsorption/desorption cycles were sequentially performed. Cr(VI) adsorption/desorption efficiency of nanoparticles undergoing four cycles is illustrated in Fig. 4. The results presented that iron oxide nanoparticles have still high ability to adsorb chromium ions after four adsorption /desorption cycles. Desorption percent is 82 % in the first cycle and 98 % in the next cycles. In fact, NaOH solution has high potential for the desorption of chromium ions from iron oxide nanoparticles. In the second cycle onwards, almost all of chromium ions have been desorbed from the nanoparticles surface, and the adsorbent has been completely regenerated.

The notable point in Fig. 4 is the sudden increase in chromium adsorption from about 55 % in the first cycle to 88 % in the second one.  $Fe_3O_4$  nanoparticles used in this study have a coating of PVP. It seems that interaction of  $Fe_3O_4$  nanoparticles coating with NaOH solution has led to an alteration in these particles, enhancing the efficiency of adsorption in the next steps. It can be postulated that increasing the surface charge of nanoparticles due to the formation of

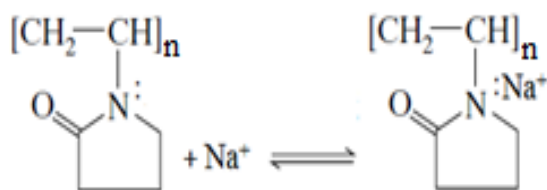
complex between PVP molecules and  $\text{Na}^+$  ions is the cause of this phenomenon. The

mechanism of complex formation of PVP/ $\text{Na}^+$  is illustrated in Fig. 5.



**Figure 4.** Regeneration study of nanoparticles after four cycles.

Nitrogen atoms (N) in the structure of PVP in sharing its lone pair electrons with the empty orbital of  $\text{Na}^+$  can create the coordination bond and adsorb  $\text{Na}^+$  ions to its surface, enhancing positively charged surface of nanoparticles and adsorption of Cr(IV), consequently.

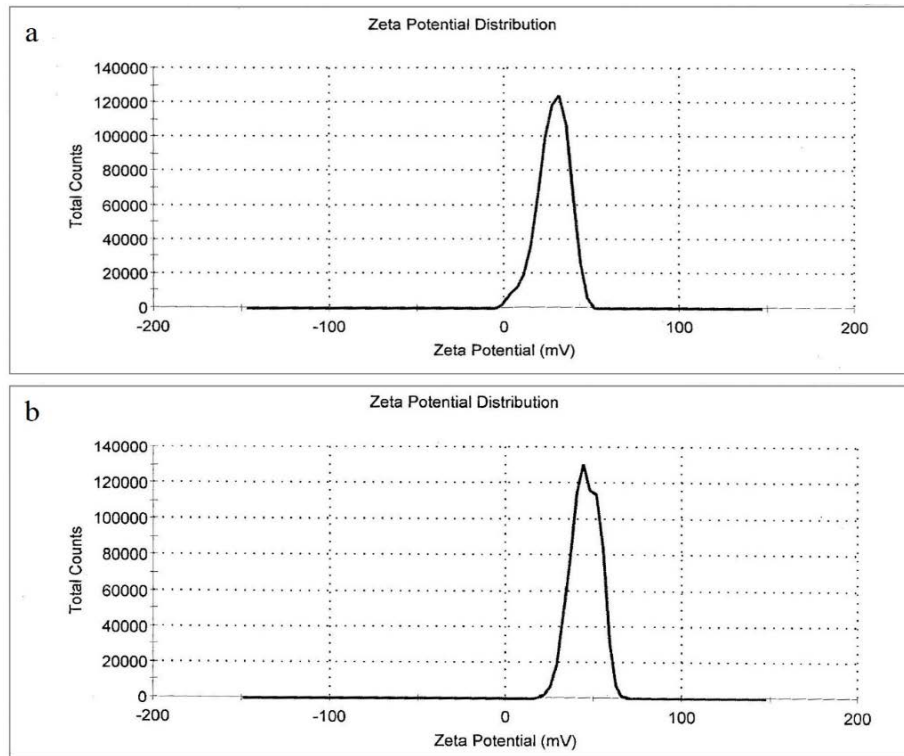


**Figure 5.** Complex formation of PVP/ $\text{Na}^+$ .

Zhang et al. and Wang et al. [23, 24] used PVP polymer as a coating for the synthesis of silver nanoparticles. Both groups of researchers believe that the donated lone pair of Nitrogen and Oxygen atoms in the polar groups of one PVP unit might occupy empty orbital of  $\text{Ag}^+$  to form a complex compound. Therefore, the complex will participate in

next processes, and at the end, the silver nanoparticles with PVP coating will be formed.  $\text{Na}^+$  ions,  $\text{Ag}^+$  ones, also have an empty orbital and can be interacted with Nitrogen atoms which results in forming the complexes. In addition,  $\text{Na}^+$  is much smaller than  $\text{Ag}^+$ , and it is easier to overcome the discouragement space of PVP polymer chains and get close to N atoms.

The mechanism of adsorption of  $\text{Na}^+$  ions on the surface of iron oxide nanoparticles increases positively charged surface of nanoparticles, leading to increased electrostatic attraction forces between the iron oxide nanoparticles and chromium anions, finally resulting in the increase of adsorption. For this purpose, the zeta potential of iron oxide nanoparticles before and after being washing with a NaOH solution was measured by Zetasizer (Malvern, zen3600) in pH 2. Fig. 6 shows the results of these analyses.

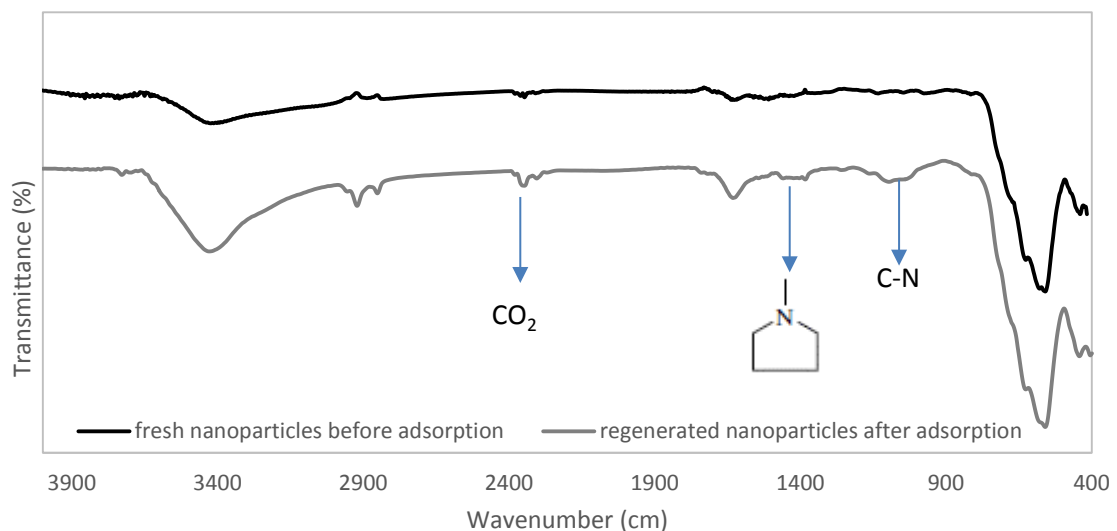


**Figure 6.** Zeta potential results a) Fresh nanoparticles and b) Washed nanoparticles with NaOH.

The results show that by washing the nanoparticles with NaOH (0.5M) solution, the zeta potential parameter is increased from  $89/7 \pm 4/29$  mV to  $91/8 \pm 6/41$  mV. An increase in zeta potential means an increase in the charged surface of nanoparticles, which confirms the proposed mechanism. Also, Fig. 6 shows that the surface charge of nanoparticles in pH 2 is positive, and this

underscores that the experiments were performed in an appropriate pH.

For further investigation, the FTIR analysis was performed on regenerated nanoparticles after chromium adsorption and compared with FTIR spectra of a fresh sample of iron oxide nanoparticles (before any adsorption), as shown in Fig. 7.

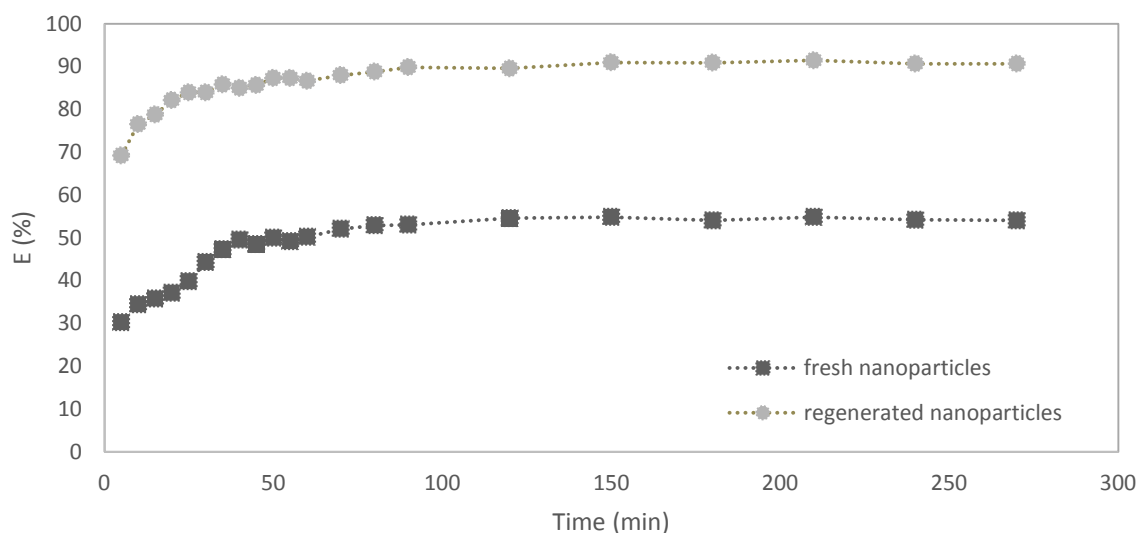


**Figure 7.** FTIR spectra of fresh and regenerated nanoparticles.

Comparing the spectra in Fig.7 shows that any additional peak is not visible. In fact, the adsorption mechanism of Cr(VI) onto regenerated  $\text{Fe}_3\text{O}_4$  nanoparticles was electrostatic attraction too, and there is not any chemical bonds between the adsorbent and adsorbate; therefore, chemical bond is not involved in any increase of chromium adsorption. However, some changes can be seen in  $1097.3\text{ cm}^{-1}$  and  $1450\text{ cm}^{-1}$  bands. These bands are due to C-N bond vibration and vibration of pentahedral ring in structure of PVP. It seems that these changes in the

molecular vibrations of the functional groups were made because of the interactions of  $\text{Na}^+$  ions and Nitrogen atoms. It should be noted that the observed band in  $2348\text{ cm}^{-1}$  probably represents the absorption of carbon dioxide in the analyzed samples.

In the following, the adsorption experiments were carried out using regenerated nanoparticles by sampling over the time. Then, the results were compared to the previous adsorption results. Fig. 8 shows the adsorption efficiency of chromium on fresh and regenerated adsorbents.



**Figure 8.** Adsorption during time using fresh and regenerated nanoparticles.

According to Fig. 8, regenerated nanoparticles are adsorbed 70 % of chromium, just in initial minutes and finally adsorption efficiency received about 90 %, while these values for fresh adsorbent are 30 % and 55 %, respectively. Although the trend of efficiency in both experiments is the same due to the similar mechanism of chromium adsorption, but amount of adsorption efficiency using regenerated nanoparticles is higher than that for fresh  $\text{Fe}_3\text{O}_4$  nanoparticles.

#### 4. Conclusions

In this study, adsorption of hexavalent chromium from aqueous solution on iron

oxide nanoparticles with PVP coating was studied in the batch system. Results show that the maximum efficiency of chromium adsorption on fresh nanoparticles is up to 55 %. Desorption process and recovery of nanoparticles using different solutions were then carried out, and it was observed that  $\text{NaOH}$  (0.5M) is able to remove 90 % of the adsorbed chromium ions. Following the completion of adsorption/ desorption cycles, it was determined that nanoparticles have still a high ability of chromium ion adsorption after 4 cycles. In addition, it was found that when iron oxide nanoparticles were washed or regenerated with  $\text{NaOH}$  solution, the



adsorption efficiency increases in the next cycle. FTIR spectra and zeta potential analysis showed that formation of a complex between  $\text{Na}^+$  ions and Nitrogen atoms in PVP structure as a coating on  $\text{Fe}_3\text{O}_4$  nanoparticles increases positively charged surface of nanoparticles, leading to an increase in electrostatic attraction forces between the iron oxide nanoparticles and chromium ions, finally resulting in adsorption increase. As a result, surface modification of iron oxide nanoparticles with NaOH solution can improve the efficiency of chromium ions adsorption.

## References

- [1] Fu, F. and Wang, Q., "Removal of heavy metal ions from wastewaters: A review", *Environmental Management.*, **92**, 407 (2010).
- [2] Wang, P. and Lo, I., "Synthesis of mesoporous magnetic  $\gamma\text{-Fe}_2\text{O}_3$  and its application to Cr(VI) removal from contaminated water", *Water Research*, **43** (15), 3727 (2009).
- [3] Alyüz, B. and Veli, S., "Kinetics and equilibrium studies for the removal of nickel and zinc from aqueous solutions by ion exchange resins", *Journal of Hazardous Materials*, **167**, 482 (2009).
- [4] Rahmani, A., Zavvar Mousavi, H. and Fazli, M., "Effect of nanostructure alumina on adsorption of heavy metals", *Desalination*, **253**, 94 (2010).
- [5] Ming, H., Zhang, Sh., Bingcai, P. and Zhang, W., "Heavy metal removal from water/wastewater by nanosized metal oxides: A review", *Journal of Hazardous Materials.*, **211–212**, 317 (2012).
- [6] Deliyanni, E. A., Peleka, K. A. and Matis, K. A., "Modeling the sorption of metal ions from aqueous solution by iron-based adsorbents", *Journal of Hazardous Materials.*, **172**, 550 (2009).
- [7] Xu, P., Zeng, G., Huang, D. and Feng, C. L., "Use of iron oxide nanomaterials in wastewater treatment: A review", *Science of the Total Environment.*, **424**, 1 (2012).
- [8] Boyer, C., Wittaker, M., Bulmus, V., Liu, J. and Davis, T., "The design and utility of polymer-stabilized iron-oxide nanoparticles for nanomedicine applications", *NPG Asia Mater.*, **2**, 23 (2010).
- [9] Dias, A., Hussain, A., Marcos, A. S. and Roque, A., "A biotechnological perspective on the application of iron oxide magnetic colloids modified with polysaccharides", *Biotechnology Advances.*, **29**, 142 (2011).
- [10] Hu, J., Chen, G. and Lo, L., "Removal and recovery of Cr(VI) from wastewater by maghemite nanoparticles", *Water Research.*, **39**, 4528 (2005).
- [11] Chowdhury, S. A. and Yanful, E. K., "Arsenic and chromium removal by mixed magnetite/maghemite nanoparticles and the effect of phosphate on removal", *Journal of Environmental Management*, **91**(11), 2238 (2010).
- [12] Wang, P. and Lo, I., "Synthesis of mesoporous magnetic  $\gamma\text{-Fe}_2\text{O}_3$  and its application to Cr(VI) removal from contaminated water", *Water Research*, **43** (15), 3727 (2009).
- [13] Pang, Y., Zeng, G., Tang, L., Zhang, Y., Lei, X. and Li, Z., "Preparation and application of stability enhanced magnetic nanoparticles for rapid removal of Cr(VI)", *Chemical Engineering Journal*, **175**, 222 (2011).
- [14] Anbia, M. and Mohammadi, N., "A fast

- and efficient method for the removal of hexavalent chromium from aqueous solutions”, *Journal of Porous Materials*, **18**, 13 (2011).
- [15] Shen, H., Pan, Sh., Zhang, Y., Huang, X. and Gong, H., “A new insight on the adsorption mechanism of amino-functionalized nano-Fe<sub>3</sub>O<sub>4</sub> magnetic polymers in Cu(II), Cr(VI) co-existing water system”, *Chemical Engineering Journal*, **183**, 180 (2012).
- [16] Badruddoza, A. Z., Shawn, Z. B. Z., Rahman, M. T., Hao, K. W., Hidajat, K. and Shahab Uddin, M., “Ionically modified magnetic nanomaterials for arsenic and chromium removal from water”, *Chemical Engineering Journal*, **225**, 607 (2013).
- [17] Yuan, P., Fan, M., Yang, D., He, H., Liu, D. and Yuan, A., “Montmorillonite-supported magnetite nanoparticles for the removal of hexavalent chromium [Cr(VI)] from aqueous solutions”, *Journal of Hazardous Materials*, **166** (2-3), 821 (2009).
- [18] Yuan, P., Liu, D., Fan, M., Yang, D., Zhu, R. and Ge, F., “Removal of hexavalent chromium [Cr(VI)] from aqueous solutions by the diatomite-supported/unsupported magnetite nanoparticles”, *Journal of Hazardous Materials*, **173** (1-3), 614 (2010).
- [19] Zhang, Z. J., Chen, X. Y., Wang, B. N. and Shi, C. W., “Hydrothermal synthesis and self-assembly of magnetite (Fe<sub>3</sub>O<sub>4</sub>) nanoparticles with the magnetic and electrochemical properties”, *Journal of Crystal Growth*, **310** (24), 5453 (2008).
- [20] Lee, H. Y., Lim, N. H., Seo, J. A., Yuk, S. H., Kwak, B. K. and Khang, G., “Preparation and magnetic resonance imaging effect of polyvinylpyrrolidone-coated iron oxide nanoparticles”, *Journal of Biomedical Materials Research*, **79B** (1), 142 (2006).
- [21] Zhang, Z., Zhao, B. and Hu, L., “PVP protective mechanism of ultrafine silver powder synthesized by chemical reduction processes”, *Solid State Chemistry*, **121**, 105 (1996).
- [22] Huang, S. H. and Chen, D. H., “Rapid removal of heavy metal cations and anions from aqueous solutions by an amino-functionalized magnetic nano-adsorbent”, *Journal of Hazardous Materials*, **163**, 174 (2009).
- [23] Pang, Y., Zeng, G., Tang, L. and Zhang, Y., “Preparation and application of stability enhanced magnetic nanoparticles for of Cr(VI)”, *Chemical Engineering Journal*, **175**, 222 (2011).
- [24] Wang, H., Qiao, X., Chen, J., Wang, X. and Ding, S., “Mechanisms of PVP in the preparation of silver nanoparticles”, *Materials Chemistry and Physics*, **94**, 449 (2005).